15

CLAIMS

A process for preparing polymers, characterized by bringing into contact:

- at least one ethylenically unsaturated monomer,
- 5 at least one source of free radicals, and
 - at least one compound of general formula (IA), (IB), or (IC):

$$S$$

$$C - S - R^{1}$$

$$R^{2} - O$$
(IA)

$$R^{2} - (-O - C - S - R^{1})_{p} \qquad (IB)$$

$$II$$

$$S$$

$$R^{1'}$$
 $S - C - O - R^{2}$)_p (IC)

in which:

10 - R^2 and R^2 , #epresent:

- an alkyl, acyl, aryl, alkene, or alkyne group
 (i), or
- a carbocyclic system (ii), saturated or unsaturated, optionally aromatic, or
- a heterocyclic system (iii), saturated or unsaturated,

these groups and cyclic systems (i), (ii), and (iii) being substituted by at least one fluorine atom, chlorine atom, and/or bromine atom, - R1 and R1' represent:

5 • an alkyl, acyl, aryl, alkene, or alkyne group (i), optionally substituted,

or

• a darbocyclic system (ii), saturated or unsaturated, optionally substituted or aromatic,

or

• a heterocyclic system (iii), saturated or unsaturated, optionally substituted, where these groups and cyclic systems (i), (ii) and (iii) may be substituted by substituted phenyl groups, substituted aromatic groups, or: alkoxy¢arbonyl or aryloxycarbonyl (-COOR), carbox $\sqrt{-COOH}$, acyloxy $(-O_2CR)$, carbamoyl (-CONR₂), cyano (-CN), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidimo, hydroxyl

(-OH), amino (-NR₂), halogen, allyl, epoxy, alkoxy OR), S-alkyl, or S-aryl groups, groups 25 having hydrophilic or ionic character, for example the alkali metal salts of carboxylic acids, the alkali metal salts of a sulfonic

10

15

20

5

acid, polyalkylene oxide chains (PEO, PPO), or cationic substituents (quaternary ammonium salts),

R representing an alkyl or aryl group, ora polymer chain,

- p is between 2 and 10.
- The process as claimed in the preceding claim, characterized in that R^2 and R^2 , are substituted by at least one fluorine atom.
- 3. The process as claimed in any one of the preceding claims, characterized in that R^2 represents a group of formula: $-CH_2R'^5$, in which R'^5 represents an alkyl group substituted by at least one fluorine atom, chlorine atom, and/or bromine atom.
- 15 4. The process as claimed in the preceding claim, characterized in that R^2 is selected among the following groups:
 - CH₂CF₃,
 - CH₂CF₂CF₂CF₃
- 20 $CH_2CH_2C_6$ \mathbb{R}_{13} .

25

- The process as claimed in any one of the preceding claims, characterized in that R^1 represents:
- a group of formula CR' 1R' 2R' 3, in which:
 - R' 1, R' 2 and R' 3 represent the groups (i), (ii), or (iii) as defined above, or
 - $R'^{1} = R'^{2} = H$ and R'^{3} is an aryl, alkene, or alkyne group,

- or a -COR 4 group in which R 4 represents a group (i), (ii), or (iii).

6. The process according to the preceding claim, characterized in that R^1 is selected among the groups:

- CH (CH₃) (CO₂Et)

- CH (CH₃) (C₆H₅)

- CH (CO₂Et)₂

- $C(CH_3)$ (CO_2Et) ($S-C_6H_5$)

10 - $C(CH_3)_{12}^{1/2}(C_6H_5)$

7. The process as claimed in any one of the preceding claims, characterized in that the

15 polymerization uses a compound of formula (IA).

8. The process as claimed in the preceding claim, characterized in that the compound of formula(IA) is selected among ethyl a-(O-heptafluorobutylxanthyl)propionate

20 $(R^1 = CHCH_3(CO_2Et), R^2 = CH_2CF_2CF_2CF_3)$, ethyl a-(O-trifluoroethylxanthyl)propionate $(R^1 = CHCH_3(CO_2Et), R^2 = CH_2CF_3)$, and ethyl a-(0)-tridecafluorooctanylxanthyl)propionate $(R^1 = CHCH_3(CO_2Et), R^2 = CH_2CH_2C_6F_{13}).$

- 9. The process as claimed in any one of the preceding claims, characterized in that the ethylenically unsaturated monomer is selected among: styrene or its derivatives, butadiene, chloroprene, (meth)acrylic esters, and vinyl nitriles.
- 10. The process as claimed in any one of the preceding claims, characterized in that the

 ethylenically unsaturated monomer is selected among vinyl acetate, vinyl Versatate®, and vinyl propionate.
- 11. A polymer obtainable by the process which consists in bringing an ethylenically unsaturated monomer into contact with a source of free radicals and 15 a compound of formula (IA), (IB), or (IC).
 - 12. The polymer as claimed in the preceding claim, characterized in that it has a polydispersity index of at most 2, preferably of at most 1.5.
- 13. A process for preparing multiblock
 20 polymers, characterized in that the implementation of
 the process as claimed in one of claims 1 to 10 is
 repeated at least once, using:
 - compared with the preceding implementation, different monomers, and
- 25 instead of the precursor compound of formula (IA), (IB), or (IC), the block polymer from the preceding implementation.

- 14. A block polymer obtainable by the process as claimed in the preceding claim.
- 15. The block polymer as claimed in the preceding claim, characterized in that it has an index of polydispersity of at most 2, preferably of at most 1.5.
 - 16. /The block polymer as claimed in claim 11 or 12, characterized in that it has at least two polymer blocks selected among the following partners:
- 10 polystyren#/polymethyl acrylate
 - polystyrene/polyethyl acrylate,
 - polystyrene kpolytert-butyl acrylate,
 - polyethyl acrylate/polyvinyl acetate,
 - polybutyl acrylate/polyvinyl acetate
- 15 polytert-butyl acrylate/polyvinyl acetate.

add A1>